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Direct synthesis of $Co_2Al(OH)_{7-2x}(CO_3)_x \cdot nH_2O$ layered double hydroxide nanolayers by successive ionic layer deposition and their capacitive performance

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ABSTRACT

New method of synthesis of $Co_2Al(OH)_{7-2x}(CO_3)_x \cdot nH_2O$ layered double hydroxide (LDH) films by successive ionic layer deposition (SILD) is presented in this paper. The obtained nanolayers were characterized by SEM, EDX, XRD, XPS, FTIR spectroscopy and electrochemical techniques. The results showed that the as-synthesized product is formed by nanosheets with a thickness of 3–5 nm, having hydrotalcite crystal structure. Electrochemical characterization of the sample prepared by 50 cycles of SILD indicated a capacitive behavior with the specific capacitance value of 900 F/g at a current density of 1 A/g and 950 F/g at 0.5 A/g in 1 mol/L KOH aqueous solution. Repeated cycling for 1000 charge–discharge cycles demonstrate that capacitance increases by 6%, so such electrodes may be used as electrodes of hybrid supercapacitors. The presented convenient route of synthesis may be used for the preparation of LDH films with high surface area and a large capacitance.

1. Introduction

Supercapacitors, also known as electrochemical capacitors, electrochemically store and deliver energy at high charge–discharge rates and are a key emerging technology for energy storage. In general, supercapacitors can be classified into two types according to their energy storage mechanism: electrical double layer capacitor and pseudocapacitors, depending on whether Faradaic redox reactions exits or not during the charge and discharge process [1]. Faradaic processes allow pseudocapacitors to achieve greater capacitances (10–100 times higher) and energy densities than electrical double layer capacitor.

As electrode materials for pseudocapacitor have been widely used few kinds of materials include MnO_2 [2,3], RuO_2 [4], MoO_3 [5], NiO and $Ni(OH)_2$ [6,7], Co_3O_4 and $Co(OH)_2$ [8–10], etc.

Recently, layered double hydroxides (LDHs) began to attract attention as a new electrode materials for supercapacitors. A general formula for LDHs may be written as $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2][A^{n-}]_{x/n} \cdot zH_2O$, where M^{2+} may be cations of Mg^{2+}, Co^{2+} or Ni^{2+} and M^{3+} may be Al^{3+}, Fe^{3+}, or Cr^{3+}, etc. and A^{n-} can be an interlayer anion, e.g. $CO_3{}^{2-}$, $SO_4{}^{2-}$, $NO_3{}^{2-}$. Currently, the chemistry of LDH is well studied and they have a wide application as catalysts, adsorbents, ion exchange, optical and magnetic materials, drug delivery systems and electrodes components for chemical power sources and sensors [11].

Among LDHs the most promising for the creation of new supercapacitors are layers containing cations of Co^{2+}, for example $Co_2Al(OH)_7 \cdot nH_2O$. Previously, the electrochemical properties of electrodes of this composition were examined for a sample obtained by precipitation [12], hydrothermal [13,14] and refluxing [15] methods. It was shown that the capacitance of supercapacitors based on these electrodes is in the range from 263 to 641 F/g at a current density of 1 A/g.

New possibilities of thin film LDH synthesis rose after development of Layer-by-Layer (LbL) synthesis techniques that make possible to deposit LDH layers on the surface of samples with irregular shape, providing exact thickness of the layer [16]. The LbL methods have advantages compared to the more conventional coating methods, in particular the simplicity of the LbL process and equipment, the flexible application to objects with irregular shapes and sizes and control over the required multilayer thickness [17]. The reagents to LbL synthesis commonly been used are colloidal nanoparticles, charged inorganic substances, heteropolyacids, and polyelectrolyte solutions. The LbL provides a simple method for preparing thin-film electrodes for electrochemical capacitors [18].

One of the methods of LbL synthesis is the SILD method [19–21] or in other terminology Successive Ionic Layer Adsorption and

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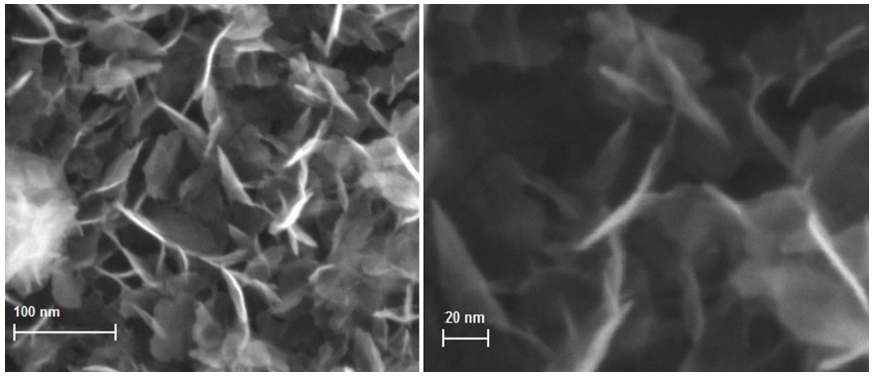

Fig. 1. SEM images of $Co_2Al(OH)_{7-2x}(CO_3)_x \cdot nH_2O$ layer on silicon.

Reaction (SILAR) [22]. The synthesis of SILD method is performed without the use of polyelectrolyte solutions and this makes it possible to simplify the procedure significantly and get the coating that contain only inorganic compounds, which is important for many tasks.

In this study, on example $Co_2Al(OH)_{7-2x}(CO_3)_x \cdot nH_2O$, we report about new simple route of synthesis of LDH by SILD method, using solutions of salt cobalt and aluminum, and its application to supercapacitors electrode materials.

2. Experimental

As a substrate for nanolayers synthesis 5 mm × 25 mm polycrystalline nickel foam (NF) plates (110 PPI) were used, on which electrochemical experiments were preformed, and also 10 mm × 25 mm × 0.35 mm single-crystal silicon plates with ⟨1 0 0⟩ orientation, were used for physical characterization. Extra pure water (Milli-Q) was used in all experiments. Substrates of silicon were cleaned in an ultrasonic bath filled with acetone for 10 min. Then plates were sequentially treated for 10 min in concentrated HF, water, 70% HNO_3, water, 0.1 M KOH and than flushed out by water. NF plates were treated according to the technique described in [23] for 15 min in 6 M HCl solution, then several times rinsed by water and dried on air at 120 °C for 30 min.

The reagents used for synthesis were aqueous 0.01 M solutions of analytical grade $Co(NO_3)_2 \cdot 6H_2O$ (pH 6.5) and $Al(NO_3)_3 \cdot 9H_2O$ (pH 9.5). pH of these solutions was controlled by addition of NaOH solution. The time between the preparation of solutions and synthesis of nanolayers was 1 h.

For synthesis of LDH substrate nickel foam plates were fixed in a holder of special home made automatic setup and sequentially immersed for 30 s into solution of cobalt salt, further in water, solution of aluminum salt and again in water. The sequence corresponds to one SILD cycle, which is repeated 50 times to obtain the desired film thickness.

The obtained samples were characterized by SEM, EDX, FTIR, XRD, and XPS methods. The morphology and composition of synthesized films were investigated by SEM at accelerating voltage of 5 kV on Zeiss Merlin microscope equipped with an EDX spectrometer (Oxford INCAx-act). FTIR transmission spectra of synthesized films on silicon surface were registered by Shimadzu IR Prestige-21 spectrophotometer using differential technique with respect to spectra of bare silicon plate. XRD patterns were obtained using a Bruker D8 DISCOVER X-ray diffractometer with CuK_α radiation in grazing incidence diffraction geometry ($\theta = 0.3°$). X-ray photoelectron spectroscopy of sample (XPS) was obtained using ESCALAB 250Xi electron spectrometer, with Al Kα radiation (14,866 eV).

All electrochemical measurements of electrodes with synthesized films were made by Elins P-30I potentiostat using a three-electrode cell with 1 mol/L KOH solution as an electrolyte. Platinum plate and Ag/AgCl (aq. KCl sat.) were used as counter electrode and reference electrode, respectively. Electrochemical characterization of the films was made by cyclic voltammetry and galvanostatic charge–discharge techniques. Cyclic voltammograms were recorded at different scan rates of 5, 10 and 20 mV s^{-1} with a potential sweep range between 0 and 0.55 V.

Specific capacitance C of a nickel foam electrode with LDH layer was determined according to [24] as:

$$C = \frac{I}{(\Delta V/\Delta t)m},$$

where I (mA) is a galvanostatic current, ΔV (mV) is the potential window, Δt (s) is the discharge time of a cycle and m (g) is the mass of the active material in the film electrode. LDH formation on nickel surface was controlled by OHAUS Pioneer™ PA54C precise balance.

3. Results and discussion

The SEM images of the Co-Al LDH layers are shown in Fig. 1. As can be seen, the Co-Al LDH layers are formed of nanosheets with a thickness of 3–5 nm.

Energy dispersive X-ray spectra analysis (EDX) (Fig. 2) show significant energy signal intensity of the Co, Al, O and C elements in the LDH nanolayers. The atomic concentration ratio of Co/Al is equal to 2:1.

The X-ray diffraction (XRD) patterns of the LDH film is shown in Fig. 3. The series of diffraction peaks of (0 0 3), (0 0 6), (0 1 2), (0 1 5)

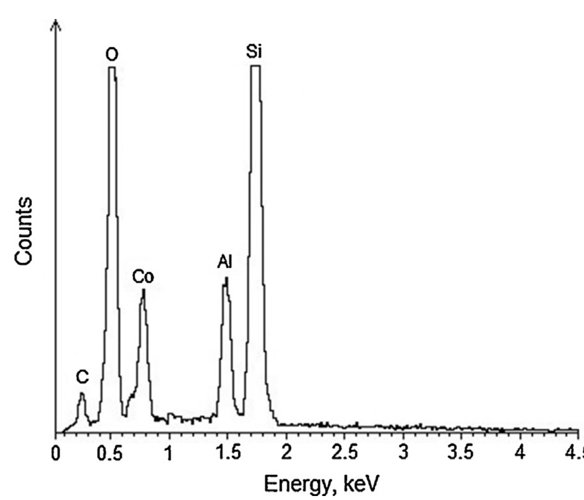

Fig. 2. EDX spectrum of $Co_2Al(OH)_{7-2x}(CO_3)_x \cdot nH_2O$ layer on silicon.